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FIELD CAPTURE OF NORTHERN AND WESTERN CORN ROOTWORM BEETLES RELATIVE TO ATTRACTANT STRUCTURE AND VOLATILITY

LESLIE HAMMACK[1,*] and RICHARD J. PETROSKI[2]

[1]*USDA-ARS Northern Grain Insects Research Laboratory*
2923 Medary Ave., Brookings, South Dakota 57006, USA

[2]*USDA-ARS National Center for Agricultural Utilization Research*
1815 N. University St., Peoria, Illinois 61604, USA

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Abstract—We used field assays to study attraction of feral northern and western corn rootworm beetles (*Diabrotica barberi* and *D. virgifera virgifera*) to a series of mostly nitrogenous and benzenoid synthetic compounds allied with host plant and floral aromas. Vaporization rates were obtained for most field-tested compounds and selected additional lures under both ideal and field-representative, but constant, conditions. Although many test compounds showed at least trace activity for one or both species, methyl benzoate and some of its derivatives, notably methyl anthranilate and methyl 4-methoxybenzoate, merited emphasis as effective new lures for females. Structural alteration of methyl benzoate had consistently negative effects on northern corn rootworm captures despite variable effects on release rate, whereas western corn rootworm was more strongly attracted to methyl anthranilate and methyl 4-methoxybenzoate than to the considerably more volatile parent compound. Phenylacetaldoxime was attractive to females of both species, but no more so than *syn*-benzaldoxime, included as reference. Release rate was disproportionately low for benzaldoxime, as well as other nitrogenous lures, under field compared with ideal conditions. The attractiveness of salicylaldoxime to northern corn rootworm, despite its low field release rate, and the unattractiveness of methyl salicylate, having a methyl ester in place of the oxime group, similarly highlighted importance of the oxime moiety for reactivity of this species.

Key Words—*Diabrotica barberi*, *Diabrotica virgifera virgifera*, corn rootworm, kairomone, attractant, lure volatility, trapping, phenylacetaldoxime, methyl benzoate, methyl anthranilate, methyl 4-methoxybenzoate.

* To whom correspondence should be addressed. E-mail: lhammack@ngirl.ars.usda.gov

INTRODUCTION

Diabroticite corn rootworms are key pests of maize, *Zea mays* L. Crop injury in the Midwest corn belt of the United States derives mostly from larval root feeding by northern and western corn rootworm, *Diabrotica barberi* (Smith and Lawrence) and *D. virgifera virgifera* (LeConte), respectively. Western corn rootworm was also introduced into Europe in the 1990s, where its spread poses a growing threat to maize production (Enserink, 1999). Both species prefer to feed as adults on pollen, silks, and young kernels of maize (Branson and Krysan, 1981), providing the potential for additional crop damage at high pest density. Western corn rootworm utilizes maize foliage when the preferred foods become unavailable, whereas northern corn rootworm visits a variety of flowering forbs seeking pollen (Branson and Krysan, 1981; Metcalf and Lampman, 1997). Adults also exploit blossoms of cucurbits, descendents of hypothetical ancestral diabroticite hosts, when available (Metcalf and Metcalf, 1992). Host plant volatiles from both maize and cucurbit blossoms, a number of their analogs, and some floral odorants attract adults in species characteristic patterns (Lance, 1993; Metcalf and Lampman, 1997; Hammack, 2003; references in each citation). These compounds have potential applications in pest population monitoring and control via such tactics as mass annihilation of reproductive adults, especially given the strong bias toward female captures.

A previous study showed that *syn*-benzaldoxime attracted both northern and western corn rootworm (Hammack, 2001). The oxime attracted about twice as many *D. barberi* of both sexes as did cinnamyl alcohol, a potent northern corn rootworm lure of cucurbit blossom origin (Metcalf and Lampman, 1989a). This oxime was initially tested because of its structural similarity to two benzenoid lures: 2-phenyl-1-ethanol, released by maize and cucurbit blossoms and moderately attractive to both rootworm species, and 2-phenyl-1-ethylamine, an effective northern corn rootworm attractant (Metcalf and Lampman, 1991) not known from host plants but apparently acting synergistically with the alcohol and active enough to alter beetle distributions within maize fields before most females would have oviposited (Petroski and Hammack, 1998; Hammack, 2003). Neither the oxime nor the amine is reported from host plants of diabroticites, but a related compound, phenylacetaldoxime, is common in floral aromas (Kaiser, 1991; Knudsen et al., 1993).

Volatility estimates obtained by measuring release rates from thin films on aluminum planchets are available for some diabroticite lures of squash-blossom origin or their structural analogs (Metcalf and Lampman, 1991; Metcalf and Metcalf, 1992). Most studies of kairomones affecting *Diabrotica* adult behaviors, however, dispense test compounds from cotton wicks, and lure release rates are generally unavailable for cotton dispensers despite their widespread use (Metcalf and Metcalf, 1992; Lance, 1993; Metcalf et al., 1995; Ventura et al., 2000; Hammack, 2003; references in each citation).

Here, we evaluated attraction of feral northern and western corn rootworm beetles to benzaldoxime compared with phenylacetaldoxime and to a series of typically nitrogenous and/or benzenoid synthetic compounds structurally related to the oximes or to methyl benzoate. Volatility and release rate data were obtained for most of the candidate attractants, as well as for several compounds previously shown to be attractive when vaporized from cotton-wick dispensers, to facilitate evaluation.

METHODS AND MATERIALS

Candidate Attractants. Source and purity of test compounds are listed in Table 1, except for phenylacetaldoxime. The oxime was synthesized from phenylacetaldehyde and hydroxylamine hydrochloride, as per Vogel (Furniss et al., 1989). Purity was determined to be >95% (GC analysis) after recrystallization (3×) from benzene–hexane.

Volatility and Release Rate Determinations. Test compound volatility was determined gravimetrically using the rate of weight loss from a 20-mg loading dose in 100–200-μl acetone dispersed over aluminum planchets exposed in a laboratory hood at a wind speed of about 45 m min^{-1}, as detailed by Metcalf and Lampman (1991). Nominal release rate from cotton-wick dispensers was determined under the same conditions but at higher loading dose (Table 1) or over a dosage range (Table 2), and only solids were applied in solvent, as described below for the field experiments. Release from cotton dispensers was also measured at 20–23°C, 2–3°C cooler than that from aluminum. Cotton wicks were obtained from Patterson Dental Supply Co. (Minneapolis, MN, No. 085-0073 cotton rolls, 1-cm diam. × 3.8-cm long). Controls for possible weight change of the absorbent dispensers due to changes in relative humidity during testing were also included, as previously described (Hammack, 2003). Weight loss determinations were replicated four times for each dispenser type and dosage. Slopes of lines relating mean weight of volatile-treated dispensers with time after treatment were used to estimate compound volatility and nominal release rates.

Bioassays and Experiments. Attractiveness of test chemicals to northern and western corn rootworm beetles was assessed using beetle captures on baited and unbaited yellow sticky traps (Pherocon AM, Trécé Inc., Salinas, CA) wrapped around maize plants at about ear height in commercial maize fields in Brookings County, SD. Compounds solid below 35°C were dissolved in 100–200-μl ethanol, or acetone in the case of indole, before application to the cotton dispensers used in all field trials. All dispensers on traps within tests received the same solvent

TABLE 1. TEST CHEMICAL SOURCE, PURITY AND RELEASE RATE BY DISPENSER LOADING DOSE AND TYPE

Chemical	Source/purity (%)	Release rate (μmoles hr^{-1})		
		20 mg on aluminum	100 mg on cotton	600 μmoles on cotton
Methyl benzoate	Aldrich/99	286.45	133.44	108.29
Phenyl acetate	Aldrich/99	175.78	—	56.50
Methyl 2-methylbenzoate	Aldrich/99	125.09	58.33	—
Ethyl benzoate	Aldrich/>99	126.99	—	54.54
Benzyl acetate	Aldrich/>99	74.34	—	37.92
Methyl 4-methylbenzoate	Aldrich/>99	119.19	—	34.83
Propyl benzoate	Aldrich/99	37.47	31.47[a]	31.47
Methyl salicylate	Aldrich/>99	168.26	33.28	28.35
Methyl phenylacetate	Aldrich/>99	78.65	—	25.64
Ethyl phenylacetate	Aldrich/>99	40.91	21.58[a]	21.58
2-Phenethyl acetate	Fluka/≥99	30.00	16.66[a]	16.66
2-Phenyl-1-ethanol	Aldrich/99	37.37	13.30	—
β-Caryophyllene	Fluka/99	20.44	11.55	—
Geranylacetone	Fluka/>98	8.40	4.04	—
Indole	Aldrich/>99	39.33	3.46	—
Methyl anthranilate	Aldrich/>99	13.37	2.53	2.59
syn-Benzaldoxime	Fluka/99	24.27	2.17	—
Ethyl *trans*-cinnamate	Aldrich/99	6.08	2.10	2.41
Methyl 2-methoxybenzoate	Aldrich/99	5.74	1.94[a]	1.94
Methyl 4-methoxyphenylacetate	Aldrich/97	2.89	—	1.03
Methyl 4-methoxybenzoate	Aldrich/99	9.24	0.89[a]	0.89
Salicylaldoxime	Aldrich/98	2.44	0.43	—
Cinnamyl alcohol	Aldrich/98	1.93	0.94	—
4-Methoxycinnamaldehyde	Schw[b]/≥98	0.15	0.07	—
(±)-Linalool	Aldrich/97	184.11	—	—
2-Phenyl-1-ethylamine	Aldrich/>99	102.93	—	—
(+)-α-Terpineol	Fluka/99	55.94	—	—
β-Ionone	Aldrich/96	0.16	—	—
Methyl 4-aminobenzoate	Aldrich/98	0.04	—	—
Methyl 2-nitrobenzoate	Aldrich/98	—	—	—
Methyl 4-methoxysalicylate	Aldrich/98	—	—	—
2,1-Benzisoxazole	Aldrich/99	—	—	—
1,2-Benzisoxazole	Aldrich/95	—	—	—
Pyrrole	Aldrich/98	—	—	—
Acetone	Aldrich/>99.5	—	—	—
Hexane	Aldrich/>99	—	—	—

[a]Estimated from the 600 μmole treatment weighing 97.5 ± 2.2 mg.
[b]Schweizerhall, Inc. South Plainfield, NJ.

TABLE 2. RELATIVE RELEASE RATE FOR SELECTED ATTRACTANTS AS A FUNCTION OF DOSE APPLIED TO COTTON DISPENSERS (RATE IN μmoles hr^{-1})

Attractant	Dose (mg dispenser^{-1}) 10	30	100
Methyl benzoate	0.24	0.40	1 (133.44)
Methyl salicylate	0.31	0.56	1 (33.28)
2-Phenyl-1-ethanol	—	0.44	1 (13.30)
β-Caryophyllene	0.36	0.64	1 (11.55)
Methyl anthranilate	0.41	0.64	1 (2.53)
syn-Benzaldoxime	0.28	0.52	1 (2.17)
Ethyl *trans*-cinnamate	0.29	0.49	1 (2.10)
Salicylaldoxime	0.67	0.86	1 (0.43)

quantities, but none of the extender that was previously employed (Hammack, 1996, 2001). Traps were separated from each other and field edges by 30 m or more. Maize phenology and beetle number per plant were estimated on the last day of each test from 40 plants spread throughout test areas but located about midway between trap sites. Traps were returned to the laboratory where captured corn rootworm beetles were counted by species and sex. Chemicals were deemed olfactorily attractive if they caught significantly more beetles than did a control.

Each of three field experiments was laid out in a randomized complete block design with six replicates. A 1997 test compared beetle responses to *syn*-benzaldoxime and phenylacetaldoxime at dispenser loading doses from 1 to 300 mg. A 1998 test examined responses to methyl benzoate, to a series of its derivatives, and to nitrogenous compounds structurally related to this ester or to the oximes. The 1997 and 1998 tests each lasted 48 hr. A shorter duration test deployed for 24 hr in 2000 further examined effects of functional group additions to the methyl benzoate ring and modification of its side chain. Dispenser loading dose was 100 mg in the 1998 test but changed to 600 μmoles in 2000. An equimolar loading dose would theoretically ensure an olfactory stimulus of quantitatively equivalent strength for compounds of similar volatility but different molecular weight.

Statistical Analysis. Data analyses used SAS statistical software (SAS Institute, 1989). Linear regression analysis calculated the slope of lines describing rate of loss of test compounds from dispensers. For each species and sex within field tests, trap capture data were transformed [$\ln(x + 1)$] to meet the assumption of variance homogeneity before using analysis of variance (ANOVA) to test the null hypothesis of no difference in captures among lure treatments. A Student–Newman–Keuls test separated means after a significant ANOVA ($P \leq 0.05$). Figures show untransformed data.

RESULTS

Volatility and nominal release rate data obtained for most attractants examined here and for a few lures tested previously, including cinnamyl alcohol, geranylacetone, and linalool (Hammack 1996, 2001), showed that release rates from cotton, while slower, generally tended to correlate with those from aluminum planchets, as expected (Table 1). However, there were notable exceptions. Most striking, a switch from aluminum to cotton reduced rates disproportionately for all of the nitrogenous compounds (benzaldoxime, salicylaldoxime, indole, and methyl anthranilate) and for methyl 4-methoxybenzoate and methyl salicylate. A similar albeit weaker reduction occurred for phenyl acetate, methyl phenylacetate, methyl 4-methoxyphenylacetate, methyl 2-methoxybenzoate, methyl 4-methylbenzoate, 2-phenyl-1-ethanol, and ethyl *trans*-cinnamate (Table 1). As a result, the release rate of benzaldoxime from cotton was only about twice that of cinnamyl alcohol, despite the more than 10-fold difference in volatility when vaporization was from thin films on aluminum planchets.

For the attractants ordered in Table 2 from most to least volatile, release rates following application of 10, 30, and 100 mg to cotton varied to a lesser degree than did the dispenser loading doses. With the exception of salicylaldoxime, the least volatile of the test lures, the 10-fold range in loading dose resulted in a 2.4- to 4.2-fold change in release rate. Salicylaldoxime release rate varied by only 1.5 times under the same conditions. Otherwise, there was little relationship between compound volatility and the variation in release rate with change in loading dose (Table 2).

Loss of weight of cotton wicks with time after methyl anthranilate treatment (Figure 1) illustrates several key points about the determination of release rates shown in Tables 1 and 2. First, release of test volatiles occurred in the laboratory at constant linear rates that continued until wicks lost more than 70–80% of the loading dose (e.g., Figure 1, 10-mg dose) or until observation was ended after more than 48 hr, the longest field-trapping interval used here. In addition, regression analyses that generated the cotton-wick data in Tables 1 and 2 were always highly significant ($P < 0.001$) and produced r^2 values usually ≥ 0.98. Four lower r^2 values occurred: 0.91 for 4-methoxycinnamaldehyde, which was observed for only 5 d despite its very low volatility, and 0.95–0.97 for 10-mg doses of methyl benzoate, ethyl *trans*-cinnamate, and methyl salicylate.

Northern and western corn rootworm females were attracted by both benzaldoxime and phenylacetaldoxime, although only the higher phenylacetaldoxime doses attracted the latter (Figure 2). No data are shown for males because their numbers in no case differed significantly between oxime and control treatments. For females, mean captures varied significantly with dose of benzaldoxime, but only western corn rootworm showed a dose-dependent response to phenylacetaldoxime. Respective regression equations for each lure ($N = 5$), where

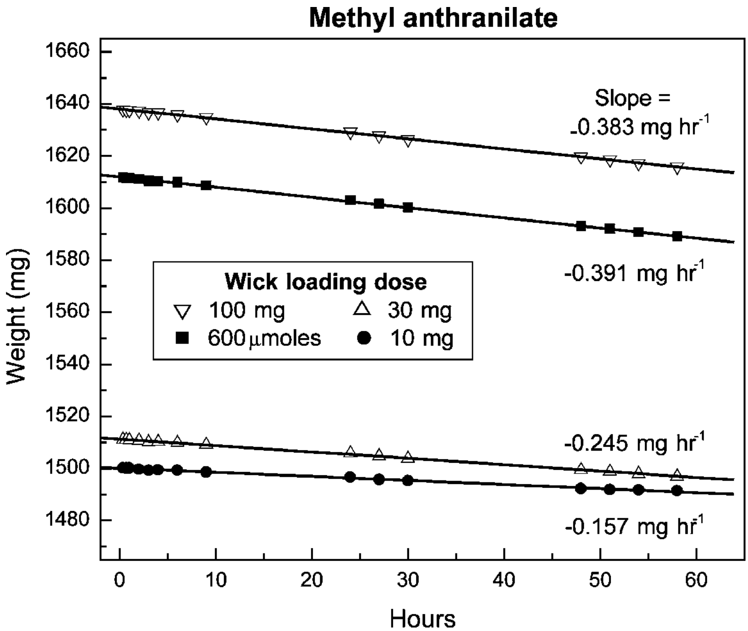

FIG. 1. Representative regression lines calculated to estimate release rates for different loading doses of compounds applied to cotton dental wicks.

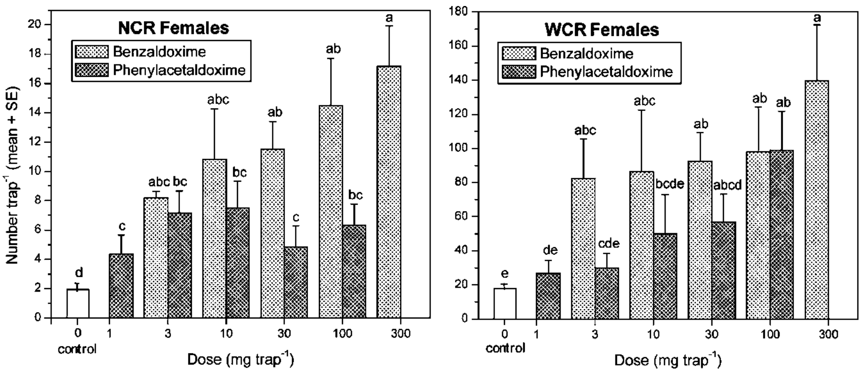

FIG. 2. Capture of female northern (NCR) and western corn rootworm (WCR) beetles after 48 hr on traps baited with benzaldoxime or phenylacetaldoxime at varied doses. Values topped by different letters differ at $P \leq 0.05$ by Student–Newman–Keuls test after ANOVA ($F_{\mathrm{NCR}} = 9.40$, $F_{\mathrm{WCR}} = 7.46$; df $= 10, 50$; and $P < 0.001$ for both species). At test end, August 28, 1997, maize was dough stage (R4) and mean beetle count per plant (±SE) was 0.7 ± 0.2 and 1.1 ± 0.2 for NCR and WCR, respectively ($N = 40$).

$x = \ln(\text{dose})$ and $y = \ln(\text{mean capture trap}^{-1} + 1)$, were $y = 0.13x + 2.06$, $r^2 = 0.99$, $P < 0.001$ (northern); $y = 0.14x + 3.96$, $r^2 = 0.77$, $P = 0.05$ (western); and $y = 0.03x + 1.76$, $r^2 = 0.09$, $P > 0.6$ (northern); $y = 0.30x + 2.97$, $r^2 = 0.95$, $P < 0.005$ (western). The increasing responses of both species to the 10-, 30-, and 100-mg doses of benzaldoxime did not differ statistically (Figure 2), despite the 4-fold increase in nominal release rate achieved with the 10-fold increase in loading dose (Table 2).

Captures on traps exposed in 1998 and baited with a nitrogenous compound or with methyl benzoate or one of its derivatives showed three compounds to be especially effective lures for northern corn rootworm females: methyl benzoate (nominal release rate of 133.4 μmoles hr^{-1}), benzaldoxime (2.2 μmoles hr^{-1}) included as a reference, and salicylaldoxime (0.4 μmoles hr^{-1}) (Figure 3). Only methyl benzoate was significantly attractive to northern corn rootworm males. Compounds included in this test but omitted from Figure 3 because they failed to capture significantly more beetles of either sex or species than did control traps were methyl 2-nitrobenzoate, methyl 4-methoxysalicylate, 2,1-benzisoxazole (anthranil), 1,2-benzisoxazole, and pyrrole. Of the three best lures, methyl benzoate attracted the most and salicylaldoxime the fewest northern corn rootworm females; however, nominal release rates, which differed markedly between methyl benzoate and the oximes, declined in the same order and methyl benzoate likely dissipated well before the end of the 48-hr test period. Functional group addition in either the 2- or 4-position of the methyl benzoate ring dramatically reduced northern corn rootworm female captures despite a highly variable effect on release rate. Rates in micromoles per hour after functional group addition were 58.3 for methyl, 33.3 for hydroxyl, 2.5 for amino, and 1.9 for methoxy groups in the 2-position and 0.9 for a methoxy group in the 4-position. Methyl anthranilate (2-amino addition) and methyl 4-methoxybenzoate were the only test compounds to retain any attractiveness to northern corn rootworm females after functional group addition to the methyl benzoate ring (Figure 3). Cotton wicks treated with methyl anthranilate tended to develop a brownish-purple discoloration during this and subsequent field trials, although not in the laboratory tests.

All of the test compounds in Figure 3, except salicylaldoxime with a release rate of 0.4 μmoles hr^{-1}, captured significantly more western corn rootworm females than did control traps, but highest captures occurred in response to methyl 4-methoxybenzoate, followed by methyl anthranilate, benzaldoxime, indole, and methyl benzoate. The only compound attractive to western corn rootworm males was methyl 4-methoxybenzoate. Replacement of its 4-methoxy with a 2-methoxy or 2-amino group decreased captures, but significantly so only for females, despite small increases in release rates (Figure 3). Addition of a 2-methyl or 2-hydoxyl group to the methyl benzoate ring also depressed captures, although less than it did for northern corn rootworm and the reductions were not statistically significant for either western corn rootworm sex (Figure 3).

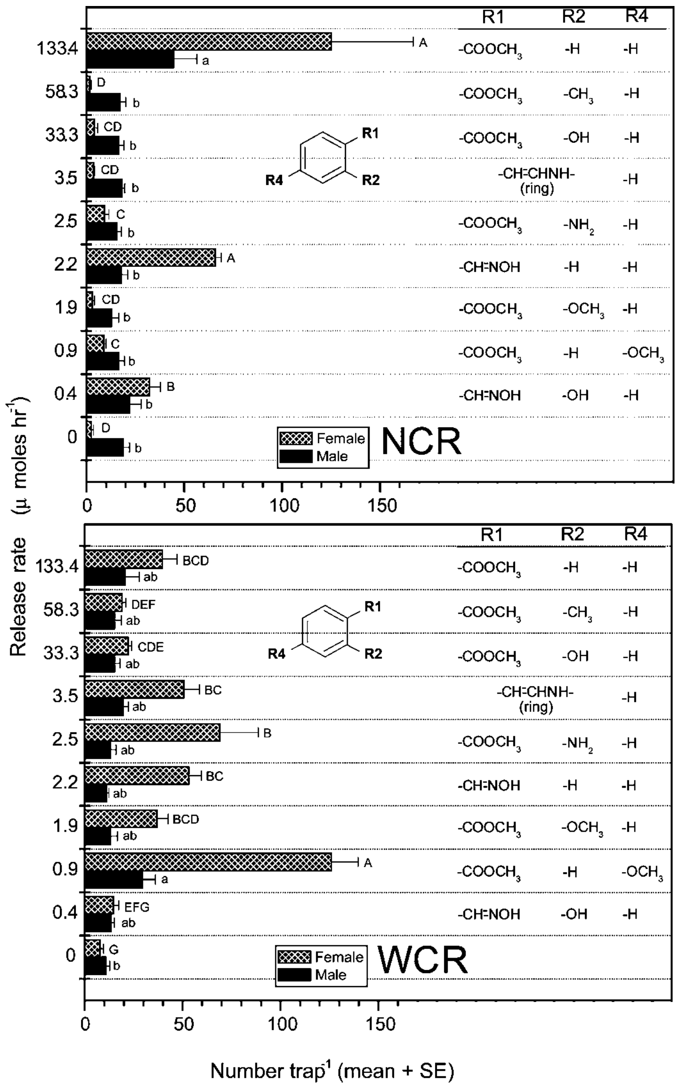

FIG. 3. Capture of northern (NCR) and western corn rootworm (WCR) beetles by sex after 48 hr in relation to lure structure and nominal release rate achieved with 100 mg on cotton dispensers. Rate 0 denotes control. Values within species and sexes topped by different letters differ at $P \leq 0.05$ by Student–Newman–Keuls test after ANOVA ($F_{\mathrm{NCR}} = 24.76$ and $F_{\mathrm{WCR}} = 17.84$ for females, $P < 0.001$; $F_{\mathrm{NCR}} = 2.48$ and $F_{\mathrm{WCR}} = 2.04$ for males, $P < 0.03$; df $= 14, 70$ for both sexes). At test end, August 27, 1998, maize was dent stage (R5) and mean beetle count per plant ($\pm$SE) was 1.7 ± 0.2 and 1.5 ± 0.2 for NCR and WCR, respectively ($N = 40$).

Functional group additions to the methyl benzoate ring or modification of its side chain generally reduced northern corn rootworm captures in 2000, when test duration was 24 hr instead of 48 hr (Figure 4). Methyl or amino addition in the 4-position obliterated attractiveness although the latter change also profoundly reduced release rate. The 2-amino and 4-methoxy additions led to lures still slightly attractive to northern corn rootworm females and, in contrast with 1998, capturing males in numbers just significantly above control. Ethyl and propyl esters of benzoic acid likewise captured significantly fewer beetles of both sexes than did the methyl ester; side-chain elongation by one carbon reduced release rates by $\leq$2-fold, probably too little to explain the lower captures (Figure 4). A striking fall in northern corn rootworm captures occurred with the methyl ester of phenyl acetic acid compared with that of benzoic acid, although release rate also fell about 4-fold (25.6 compared with 108.3 μmoles hr^{-1}). Still, it is unlikely that reduced efficacy arose entirely from the release rate drop because of its relatively small magnitude and because the 4-methoxy derivatives of these same esters also differed in attractiveness, but not in release rates (1.0 and 0.9 μmoles hr^{-1}). Phenyl acetate also captured many fewer northern corn rootworms of both sexes than did methyl benzoate, its structural isomer, with a nominal release rate about half that of the benzenoid ester (56.5 *vs.* 108.3 μmoles hr^{-1}). Despite little if any attractiveness of the acetate esters of phenol (56.5 μmoles hr^{-1}) and benzyl alcohol (37.9 μmoles hr $^{-1}$), the acetate ester of 2-phenyl-1-ethanol (16.7 μmoles hr^{-1}) was modestly attractive to northern corn rootworm females, although less so than was ethyl *trans*-cinnamate (2.4 μmoles hr^{-1}) (Figure 4). Ethyl *trans*-cinnamate captured about as many northern corn rootworms as did ethyl benzoate (54.5 μmoles hr^{-1}), but the latter much more volatile compound likely dissipated within 12 hr complicating comparison of attractant activities.

All of the compounds in Figure 4 caught significantly more western corn rootworm females than did the control, except for methyl 4-aminobenzoate with its low nominal release rate ($<$0.04 μmoles hr^{-1}). Highest captures were recorded in response to methyl anthranilate (2.6 μmoles hr^{-1}) and methyl benzoate (108.3 μmoles hr^{-1}), followed by methyl 4-methoxybenzoate (0.9 μmoles hr^{-1}), ethyl benzoate (54.5 μmoles hr^{-1}), ethyl *trans*-cinnamate (2.4 μmoles hr^{-1}), and 2-phenethyl acetate (16.7 μmoles hr^{-1}). Males responded only to methyl 4-methoxybenzoate, methyl anthranilate, and ethyl *trans*-cinnamate in numbers significantly greater than control, although many fewer males than females were captured. Western corn rootworm female captures declined with ethyl and propyl compared with the methyl ester of benzoic acid, in similarity with the northern corn rootworm response pattern (Figure 4). Also like northern corn rootworm patterns were the western corn rootworm decline in captures with phenyl acetate (56.5 μmoles hr^{-1}) compared with methyl benzoate (108.3 μmoles hr^{-1}) and the improved western corn rootworm captures with 2-phenethyl acetate (16.7 μmoles hr^{-1}) compared with phenyl or benzyl acetates (37.9 μmoles hr^{-1}).

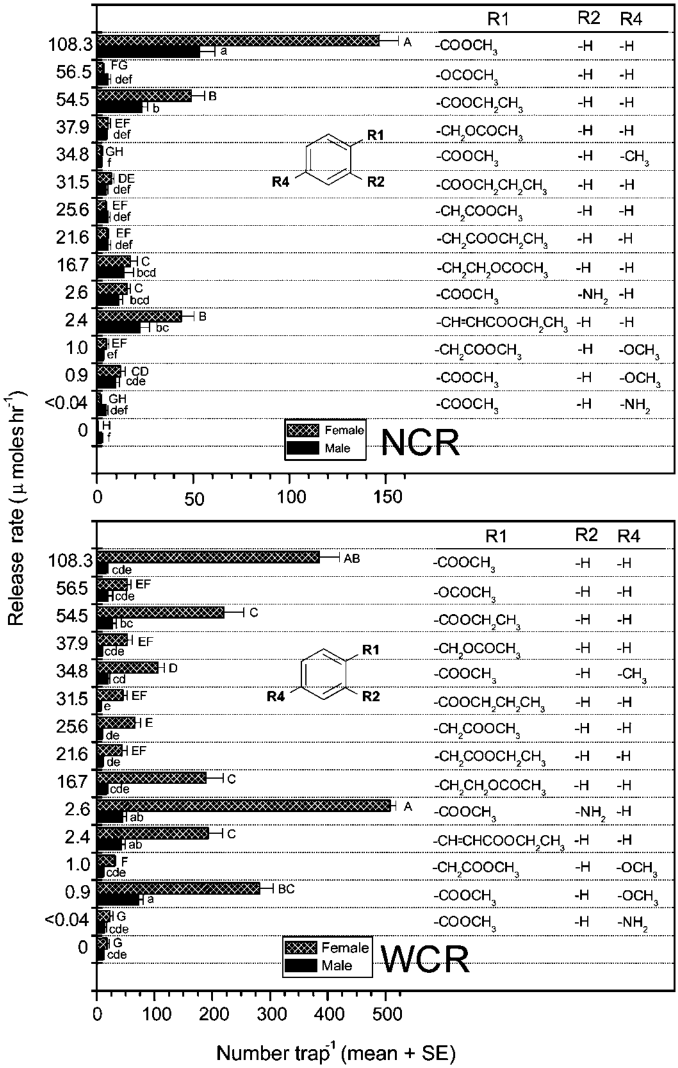

FIG. 4. Capture of northern (NCR) and western corn rootworm (WCR) beetles by sex after 24 hr in relation to lure structure and nominal release rate achieved with 600 μmoles on cotton dispensers. Rate 0 denotes control. Values within species and sexes topped by different letters differ at $P \leq 0.05$ by Student–Newman–Keuls test after ANOVA ($F_{\mathrm{NCR}} = 50.99$ and $F_{\mathrm{WCR}} = 61.26$ for females; $F_{\mathrm{NCR}} = 14.68$ and $F_{\mathrm{WCR}} = 12.02$ for males; $P < 0.001$ and df $= 14, 70$ for both sexes). At test end, August 31, 2000, maize was dough to dent stage (R4–R5) and mean beetle count per plant ($\pm$SE) was 1.8 ± 0.3 and 3.4 ± 0.5 for NCR and WCR, respectively ($N = 40$).

DISCUSSION

Our finding that benzaldoxime release rate from cotton was only about twice that of cinnamyl alcohol, deemed a potent northern corn rootworm lure (Metcalf and Metcalf, 1992), indicates that greater efficacy of the oxime than alcohol in past trials (Hammack, 2001) was not simply due to a higher oxime release rate. Female northern corn rootworm attraction to salicylaldoxime, despite its low nominal release rate (0.4 μmoles hr^{-1}), and insensitivity to the more volatile methyl salicylate (33.3 μmoles hr^{-1}) having an ester linkage in place of the oxime group, also accentuated oxime importance. Our results gave no hint that phenylacetaldoxime, at least as a mixture of stereoisomers, is any more attractive to northern or western corn rootworm beetles than is *syn*-benzaldoxime, despite the presence of the former in floral head-space volatiles (Kaiser, 1991; Knudsen et al., 1993). Fewer beetles of both species usually responded to the former, longer-chain, oxime, perhaps because of a lower release rate. We did not measure phenylacetaldoxime emission, but did show that similar one-carbon elongation of the side chain of related esters reduced nominal release rate by about 1.5- to 4-fold. This pattern manifested here for methyl benzoate (108.3 μmoles hr^{-1}) *vs.* methyl phenylacetate (25.6 μmoles hr^{-1}), phenyl acetate (56.5 μmoles hr^{-1}) *vs.* benzyl acetate (37.9 μmoles hr^{-1}), and benzyl acetate *vs.* 2-phenethyl acetate (16.7 μmoles hr^{-1}).

Our study showed that methyl benzoate and some of its structural analogs were attractive to both northern and western corn rootworm beetles, confirming earlier reports that methyl salicylate, with its 2-hydroxyl addition to the methyl benzoate ring, attracts western if not northern corn rootworm (Hammack, 2001). The methyl benzoate structure is apparently crucial for northern corn rootworm responses because various ring substitutions, side chain alterations, and a modified ester linkage all had consistently negative effects on lure efficacy despite variable effects on nominal release rates. Whereas the side chain and ester linkage changes were largely detrimental in both species, some additions at the 2- or 4-position of the methyl benzoate ring tended to maintain or improve western corn rootworm attraction. Methyl anthranilate, with its 2-amino addition, and methyl 4-methoxybenzoate, for example, were particularly effective lures given their much lower release rates than that of methyl benzoate. 4-Methoxy addition to cinnamaldehyde, more than methyl or 2-methoxy additions, likewise increased lure attractiveness to western corn rootworm, producing what is still the most effective single-component lure available for this species (Metcalf and Lampman, 1989a,b; Metcalf and Metcalf, 1992). 4-Methoxy addition to 2-phenyl-1-ethanol likewise enhanced northern corn rootworm attraction in Illinois tests (Metcalf and Lampman, 1991, 1997; Metcalf et al., 1995), but more westerly populations reacted better to 2-phenyl-1-ethanol than to its derivative (Hesler et al., 1994; Hammack, 2003), in common with northern corn rootworm response patterns seen here with methyl benzoate compared with derivatives formed by functional group additions to its ring.

Cinnamaldehyde and its derivatives are potent diabroticite attractants of cuburbit origin (Metcalf and Metcalf, 1992). Thus, the attractiveness of ethyl *trans*-cinnamate to both northern and western corn rootworm shown here is not surprising, although methyl cinnamate, a widespread floral volatile (Knudsen et al., 1993), was inactive (Metcalf and Lampman, 1989a). Ethyl cinnamate was found in vacuum distillate of maize silks (Flath et al., 1978) and as a sex pheromone constituent of emissions from lepidopteran hairpencils, where floral and fruity odors are common (Nishida et al., 1982).

Some of the relationships explored here between attractant structure and activity will need to be confirmed in additional tests in which compound release rates are equalized and, for the more volatile compounds, maintained for the entire test duration. Release of methyl benzoate, for example, likely fell off before our tests ended, as did that of several other compounds depicted in Figures 3 and 4 and showing nominal release rates greater than about 30 μmoles hr^{-1}. Lure volatilities measured here will facilitate design of these confirmatory studies, although modified dispensers will be needed to slow release of the more volatile lures to realistic levels. Methyl benzoate, for instance, is a common floral volatile (Knudsen et al., 1993) emitted from single blossoms at peak rates near 2 or 12 μg hr^{-1} (<0.1 μmoles hr^{-1}) depending on species (Kolosova et al., 2001), rates that are orders of magnitude lower than those achieved here. Another potential problem with the cotton dispensers is binding of compounds to the cotton, a possibility suggested by the slow release of some of the more polar compounds, most notably the nitrogenous ones, relative to their release from aluminum planchets. Dispensers made of inert material would prevent any such binding, but may not change release patterns if the three-dimensional cotton matrix disproportionately slowed release for some of the more polar lures not by binding them but simply by fostering more hydrogen bonding among lure molecules than occurred in the thin film on aluminum. Principles and technologies for dispensing semiochemicals are discussed by Byers (1988) and El-Sayed and Byers (2000).

Vaporization of the most volatile attractants before trapping was terminated likely caused at least one of several discrepancies between results of the 1998 and 2000 tests lasting for 48 and 24 hr, respectively. Greater western corn rootworm captures in 2000 than 1998 on traps baited with methyl benzoate, compared with lower volatility lures such as methyl anthranilate and methyl 4-methoxybenzoate, likely occurred because the former ester would have been released for a proportionately greater portion of the shorter duration test. A similar discrepancy was not evident for northern corn rootworm, but methyl benzoate was the only lure tested in both years that captured high numbers of this species. A difference between results of the two tests that cannot be so readily explained was the significantly greater attractiveness of methyl anthranilate compared with methyl 4-methoxybenzoate in 2000, but just the opposite pattern in the longer 1998 test. The discoloration of methyl anthranilate in our field trials suggested that degradation in ultraviolet light might account for its lesser efficacy in the 48- than 24-hr test; however, photolysis rate constants, at least those reported for a dilute aqueous solution in simulated sunlight (Aronov and Clark, 1996), are too low to support this explanation.

Methyl benzoate and related benzenoids, like the phenylpropanoids already implicated as an important class of corn rootworm kairomonal attractants (Metcalf et al., 1995), are synthesized *via* the shikimic acid pathway of higher plants. Terpenoid attractants such as β-ionone, linalool, and β-caryophyllene, synthesized via isoprenoid pathways, comprise another important class (Metcalf and Metcalf, 1992; Hammack, 1996, 2001). Shikimic and isoprenoid pathways, along with the octodecanoid pathway yielding green leaf volatiles not yet implicated as corn rootworm lures (Hammack, 2001), produce not only floral aromas (Dudareva and Pichersky, 2000) but also defensive volatiles induced in vegetative tissues by insect herbivory (Kessler and Baldwin, 2001). The latter may prove to be an important functional basis for attractiveness of synthetic lures to diabroticite beetles, despite their known reaction to cucurbit-blossom and maize-silk odors (McAuslane et al., 1986; Prystupa et al., 1988; Metcalf and Metcalf, 1992). Although volatile emissions induced by herbivory typically elicit herbivore damage, such volatiles may attract adult Coleoptera that aggregate on host plants for mating, mass feeding, or sequestration of defensive, secondary plant compounds (Loughrin et al., 1996; Bolter et al., 1997; Kalberer et al., 2001). Sequestration of cucurbitacins, an established activity of diabroticite beetles (Metcalf et al., 1980; Fisher et al., 1984; Eben et al., 1997), may provide a functional basis for such responses to cucurbits, if not to maize. Comparisons of beetle reactions to intact and herbivore-damaged host plants seem warranted for this reason and because of overlap, at least qualitatively, in the composition of floral, host, and herbivore-induced volatiles.

Methyl anthranilate like methyl benzoate occurs among released floral volatiles (Knudsen et al., 1993), and it is also a minor component in the headspace of vegetative maize after insect herbivory (Bernasconi et al., 1998; Turlings et al., 1998). It has been identified as an insect attractant, notably among polyphagous scarabaeid beetles (Imai et al., 1997; Maekawa et al., 1999; Larsson et al., 2003). These scarabaeids, like the diabroticites, respond to a greater or lesser degree to methyl benzoate, methyl salicylate, methyl 2-methoxybenzoate, and methyl 2-methyl benzoate, although not to ethyl or propyl benzoate in the case of the soybean beetle (Maekawa et al., 1999; Larsson et al., 2003). The first two esters, in particular, are widespread floral volatiles (Knudsen et al., 1993), and methyl salicylate is common among defensive chemicals emitted by higher plants, maize included, in response to insect herbivory (Turlings et al., 1998; Kessler and Baldwin, 2001).

Lengthening the side chain of methyl benzoate by one carbon to produce methyl phenyl acetate reduced capture of northern and western corn rootworm beetles in the present study. Such elongation of the phenyl acetate chain, however, had little effect (benzyl acetate) or, in the case of 2-phenylethyl acetate with two added carbons, significantly enhanced lure attractiveness to both species. Improvement occurred despite reduced volatility and suggested that the activity of 2-phenylethyl acetate did not arise from its structural similarity with methyl benzoate. 2-Phenylethyl acetate, like benzyl acetate, is a common floral volatile that also occurs in the headspace of vegetative maize, where it is a minor constituent above some varieties injured by insect herbivory (Takabayashi et al., 1995; Bernasconi et al., 1998; Turlings et al., 1998; Gouingueni et al., 2001, 2003) but not among herbivore-induced volatiles of the dozen or so other plant species examined to date (Fritzsche Hoballah et al., 2002). Metcalf and Lampman (1991) cited unpublished data showing lesser attractiveness of the acetates of 2-phenyl-1-ethanol and 3-phenyl-1-propanol compared with the corresponding alcohols to northern corn rootworm, but ester activity was not discussed for western corn rootworm nor has it been tested with northern corn rootworms of more westerly origin or in combination with other lures. Phenethyl esters, including 2-phenylethyl acetate, for example, contribute to the efficacy of lure blends attractive to Japanese beetles (Ladd et al., 1973).

Modest synergy has been demonstrated when lures for diabroticite beetles are dispensed in blends (Lampman and Metcalf, 1987; Metcalf et al. 1995, Hammack, 1996, 2001, 2003; Petroski and Hammack, 1998). Lure volatility and release rate data will be needed to decipher not only structure–activity relationships like those examined here but also the complex effects of qualitative and quantitative variation in the composition of multicomponent lures on the host-seeking behavior of diabroticite beetles.

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